Laser photochemical deposition of germanium-silicon alloy thin films

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Thin films of Ge-Si alloys were deposited by 193 nm photolysis of GeH_4/Si_2H_6 gas mixtures using an ArF laser. For substrate temperatures below 350 °C, deposition occurred only with the laser present, while for temperatures above 400 °C, film growth was little influenced by laser photolysis and resembled conventional chemical vapor deposition (CVD). The Si/Ge ratio in the films was about three times the $P_{Si_2H_6}/P_{GeH_4}$ ratio of reactant partial pressures for deposition in either the laser photolysis or the CVD regime. This result indicates that there is strong cross chemistry between silicon and germanium-bearing species in the gas phase. Film stoichiometry was measured by Auger analysis and Raman spectroscopy, with both methods leading to the same film composition.

The intriguing structural, electrical, and optical properties of germanium-silicon alloys can be tuned by varying the relative Ge/Si composition.[1] This fact, along with the compatibility of these compounds with existing silicon-based technology, has led to the growing number of applications of thin-film Ge-Si alloys in band-gap engineering of silicon-based microelectronic devices, solar cells, infrared detectors, and optical fiber communications.[1] Although several different techniques of depositing Ge-Si alloy films have been investigated, including pyrolytic chemical vapor deposition (CVD), and laser and plasma-assisted CVD,[2] no studies of laser photochemical vapor deposition (LPVD) of these compounds have been performed to date. The advantages of LPVD include high deposition rates at substrate temperatures lower than those characteristic of conventional CVD, decreased atomic diffusion due to low-temperature operation, and monolayer control. These latter two points are particularly important for multilayer fabrication. Investigations of excimer laser assisted LPVD of Ge-Si alloy thin films are reported here for the first time.[3,4]

Details concerning the experimental apparatus for the deposition experiments can be found elsewhere[5,6] and will only be briefly reviewed here. An ArF laser beam (193 nm, 40 Hz, 15 mJ/cm^2), filtered by a rectangular slit (0.5×2.0 cm^2), entered the quartz reactor through one wall and propagated parallel to and 2.2 mm above quartz and Si substrates. Both substrates were resistively heated ($T_s = 250$–500 °C) by an inconel heater containing a 1-mm-diam hole, which permitted the passage of a He-Ne laser beam through the quartz substrate, enabling *in situ* monitoring of the film growth by transmission. An infrared pyrometer measured the quartz surface temperature at the point where the He-Ne laser passed through the substrate.

During deposition, a disilane/germane gas mixture (diluted in a helium buffer-5% reactant gases/95% He) flowed over the substrate at a mass flow rate of 100 sccm, and a total reactor pressure of 10 Torr. The mole fraction of disilane in the gas, defined by $x_g = P_{Si_2H_6}/(P_{Si_2H_6} + P_{GeH_4})$, where $P_{Si_2H_6}$ and P_{GeH_4} are the partial pressures of disilane and germane, respectively, is taken to be a measure of the relative concentration of reactive gases. Furthermore, the total reactant pressure was fixed: $P_{Si_2H_6} + P_{GeH_4} = 0.5$ Torr. This disilane fraction x_g was varied in different experiments to grow films over the full compositional range $0 \leqslant x_f \leqslant 1$, where $x_f = [Si]/([Si] + [Ge])$ is the atomic fraction of Si in the film.

The thickness of Ge-Si films on quartz was determined by etching a trench down the center of film, and subsequently measuring the step height by profilometry. Film stoichiometry (silicon substrates) was measured by Auger electron spectroscopy (AES). Depth profiles were obtained by probing the 1147 eV Ge and 1619 eV Si peaks using 3 keV electrons directed to the center of the region that was sputtered by argon ions. Quantitative analysis was accomplished by comparing the amplitude (peak-to-peak height) of the Auger signal from the component in the alloy to the corresponding amplitude from a pure elemental standard analyzed under identical experimental conditions. Si-rich films and films grown on quartz were analyzed by x-ray photoelectron spectroscopy (XPS) using the Al K_α line.

Several AES studies of alloys have shown that backscattering of primary electrons and the escape depth of Auger electrons depend on alloy composition,[7] and that, during sputtering, the surface can be enriched by the alloy component with the lower relative sputtering yield.[8] Since these effects can influence the Auger determination of x_f, their importance in Ge-Si alloys was tested by determining the film composition of thick ~ 1-μm-thick CVD-grown films by both electron beam induced x-ray energy-dispersive analysis (EDAX) and AES. EDAX gave the same film composition as did the AES analysis, to within ± 0.02.

The stoichiometry of these thicker films was also determined by Raman scattering, using the shift of the Si-Si like peak near 500 cm^{-1}. Of the three peaks in the Ge-Si alloy Raman spectrum, the variation of the frequency of this peak with x_f is the least sensitive to the method of preparation.[2,9,10] Measurements were performed with a microprobe system (described previously),[11] and using the 5145 Å line of an Ar$^+$ laser operated at low power ($\lesssim 2$ mW, 0.6 μm spot size) to minimize substrate heating. After initial laser probing of the sample, the laser power was increased to about 40 mW for approximately 5–10 min, and then the sample was

reexamined at low power to check for the effect of annealing.

For $T_s \geqslant 400$ °C, the ArF laser was found to have only a minor impact on film growth, which occurred primarily by conventional CVD. However, below 350 °C, no film growth was observed in the absence of UV laser radiation, indicating complete laser control of growth in this experimental regime of high flow velocity (20 cm/s) and low reactant gas partial pressure (0.5 Torr). Probe transmission, monitored during the growth of photolytic films, showed that incubation times immediately preceding film growth were negligible for $x_g \gtrsim 0.005$ (< 1 min), but were significant for $x_g = 0$ (pure GeH$_4$, $\gtrsim 8$ min). Deposition rates ranged from 150 to 300 Å/min for both 250 and 350 °C substrate temperatures, and were insensitive to the disilane and germane mole fraction, with the disilane fraction $x_g \geqslant 0.1$ and with constant total reactant gas partial pressure.

Depth profiles of the photolytic films and several CVD films grown on silicon showed the composition to be independent of depth, and revealed the presence of an oxide layer at the film-substrate interface for the photolytic films despite *in situ* cleaning of the substrate with a 5% HCl/95% He gas

mixture for several minutes prior to initiating growth of the alloy.

The film composition (x_f) determined by Auger and XPS was in reasonable agreement with the Raman measurements. The Raman spectrum given in Fig. 1(a) depicts the three-peak spectrum for CVD films grown on c-Si at 500 °C with gas composition $x_g = 0.10$, and film composition $x_f = 0.45$, and indicates that the film is polycrystalline. Figure 1(b) shows the Raman profile of a film deposited under similar conditions except that $x_g = 0.90$ and $x_f = 0.91$. The broad peak shows that the as-deposited film is amorphous; the narrow peak is the result of Raman analysis after the film was converted to polycrystalline material by laser annealing. Under these conditions, the CVD films were shown to be amorphous for $x_f > 0.78$ and polycrystalline for $x_f < 0.45$ (and were not examined for intermediate x_f).

If the dissociation (and film incorporation) probability of Si$_2$H$_6$ were β times that of GeH$_4$, then it can be shown that the silicon fraction in the film (x_f) and the disilane fraction in the reactant mixture (x_g) are related by the expression

$$x_f^{\mathrm{model}}(\beta) = \frac{\beta x_g}{(\beta - 1)x_g + 1}. \tag{1}$$

In Fig. 2, the measured silicon fraction in the film (x_f) is plotted versus the right-hand side of Eq. (1) for $\beta = 3$, showing very good agreement for the photolytically grown films and relatively good agreement for the CVD films, for which $\beta \sim 5 \pm 2$. This means that the [Si]/[Ge] ratio in the photolytically grown film is enriched by a factor of 3 relative to $P_{\mathrm{Si_2H_6}}/P_{\mathrm{GeH_4}}$ (the gas phase partial pressure ratio) and a factor of 1.5 relative to the atomic [Si]/[Ge] ratio in the reactant mixture.

At 193 nm, germane is weakly absorbing with an absorption cross section of approximately 3×10^{-20} cm^2,[12] while Si$_2$H$_6$ is strongly absorbing with an absorption cross section ~two orders of magnitude larger, $\sim 2 \times 10^{-18}$ cm^2.[13] If, after laser photolysis of the reactants, there were no "cross chemistry" between Ge and Si-containing species, then β would expected to be roughly 70 or 140 based on the
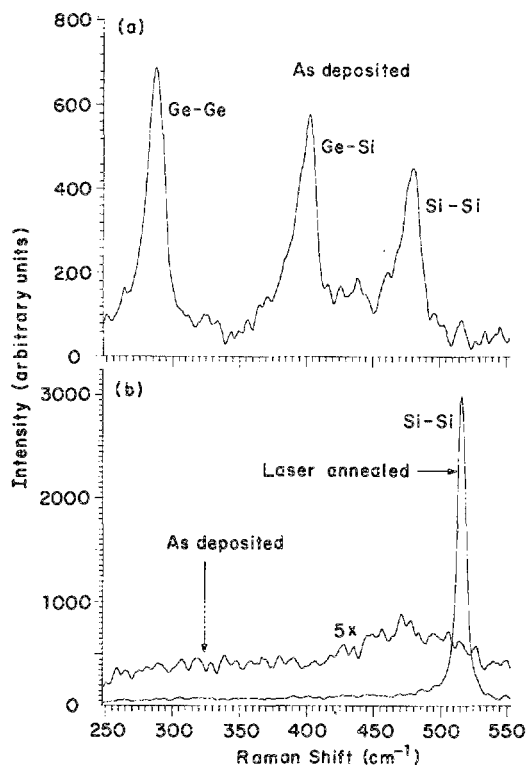

FIG. 1. Raman microprobe analysis of Ge-Si alloy thin films grown by CVD on c-Si with $T_s = 500$ °C and 1 mW of 5145 Å Ar$^+$ laser power. The Si fraction in the film (x_f) is determined by the frequency shift of the Si-Si peak. (a) Spectrum acquired for a disilane fraction in the gas mixture of $x_g = 0.10$ during deposition. Auger and EDAX measurements give $x_f = 0.45$ and 0.46, respectively, while Raman analysis gives 0.34 (using Ref. 9 for calibration) or 0.42 (using Ref. 10), depending upon the calibration curve, and shows that the as-deposited film is polycrystalline. (b) Analogous spectrum acquired for $x_g = 0.90$, with x_f determined to be 0.91 by XPS. The as-deposited film is amorphous, while the laser-annealed film (40 mW, 5 min) is polycrystalline, giving $x_f = 0.92$. For $x_g = 0.50$, x_f was measured to be 0.78 from AES, 0.80 from EDAX, and 0.76 from the Raman spectrum of the laser-annealed film (spectrum not shown). Each of the Si-Si Raman shift vs silicon fraction calibrations in Refs. 2, 9, and 10 gave the same x_f for the $x_g = 0.90$ experiment. This was also true for the $x_g = 0.50$ run.
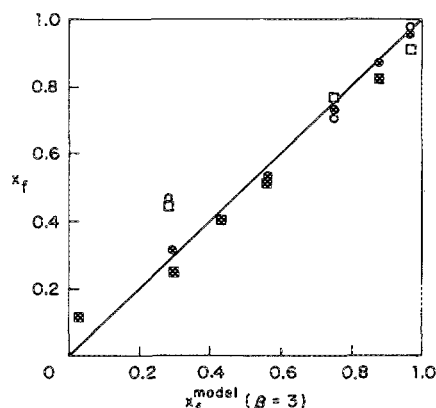

FIG. 2. Measured Si fraction of the film (x_f) as a function of x_f^{model} ($\beta = 3$) for various x_g under different experimental conditions. The solid symbols depict films grown by 193 nm photolysis at lower substrate temperatures where the laser is necessary for deposition: (circles) $T_s = 250$ °C; (squares) $T_s = 350$ °C. The open symbols depict films grown by conventional CVD at higher temperatures: (circles) $T_s = 400$ °C; (squares) $T_s = 500$ °C.

relative absorption cross sections, depending on whether only one or both of the disilane Si atoms contribute to film growth. Since the value of β for LPVD is considerably smaller, collisions between GeH_4 and Si-bearing radicals or H atoms from disilane photolysis, which form Ge-bearing radicals, undoubtedly play a pivotal role in deposition. Similar cross chemistry between Ge and Si-containing species is also likely in conventional CVD since $\beta \sim 3$ also describes the CVD-grown films fairly well. One further argument in support of the impact of cross chemistry in forming the laser-deposited films stems from the measured rate of deposition of Ge atoms, which exceeds the calculated rate at which germane molecules are photolyzed when disilane is present in the reactant mixture (specifically, for $x_g \geqslant 0.01$). For example, the Ge atom deposition rate is $8.5 \times 10^{14}/cm^2$ s during photolytic growth of Ge-Si alloy films when the disilane fraction $x_g = 0.1$ and $T_s = 350\,°C$, while the rate of photolyzing GeH_4 molecules is only $\sim 1.4 \times 10^{14}/cm^2$ s.

It appears, therefore, that deposition of the alloy is initiated by laser photodissociation of disilane, and photolysis of GeH_4 is negligible except when $x_g < 0.01$. Recent studies suggest that in the laser fluence range of these experiments, Si_2H_6 absorbs only one 193 nm photon,[14] and that the primary dissociation quantum yield is ~ 0.7.[15] At least 20 exit channels are energetically accessible in the photolysis of disilane at 193 nm.[15,16] Many of these channels may well be important, producing H, H_2, SiH_2, SiH_3, and other Si-bearing species.[15] Once formed, the silylene radical (SiH_2), for example, reacts with GeH_4 via the process $SiH_2 + GeH_4 + M \rightarrow GeSiH_6 + M$ (where M is any third body) which is analogous to the insertion reaction $SiH_2 + SiH_4 + M \rightarrow Si_2H_6 + M$ that is known to be critical to the pyrolysis of silane.[17] In addition, H atoms produced from the photodissociation of Si_2H_6 will form GeH_3 and H_2 by hydrogen abstraction from GeH_4. Since a given species formed by the laser within the photolysis zone suffers roughly 5000 collisions with background reactant molecules before reaching the surface, the nascent products of disilane photolysis are collisionally transformed by reactive collisions into the final deposition precursors, perhaps $Ge_n Si_m H_{2(n+m)}$, while en route to the surface.

In summary, low-temperature growth of Ge-Si alloy films has been demonstrated by laser LPVD. Cross reactions between Ge and Si species have been found to be important during film deposition and Raman spectroscopy has been shown to be a useful diagnostic of Ge-Si alloy film composition.

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